Experimental and Computational Studies on Stepwise [3+2]-Cycloadditions of Diaryldiazomethanes with Electron-Deficient Dimethyl (E)- and (Z)-2,3-Dicyanobutenedioates

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Experimental and Computational Studies on Stepwise [3+2]-Cycloadditions of Diaryldiazomethanes with Electron-Deficient Dimethyl (*E*)- and (*Z*)-2,3-Butenedioates

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Abstract

Electron-deficient dimethyl dicyanofumarate and dicyanomaleate react with diaryldiazomethanes at room temperature under spontaneous evolution of N_2. The type of the products strongly depends on the structure of the diazocompound. Whereas diphenyldiazomethane and its bis(4-methoxy) derivative yield cyclopropanes, sterically crowded 5-diazo-5*H*-dibenzo[*a*,*d*]cycloheptane derivatives afford either the dimer of the carbene formed via N_2 elimination or the adduct of the carbene onto the starting diazo compound. The course of the studied reactions is rationalized by stepwise mechanisms initiated by the formation of a C–N bond. A cascade of reactions leads to the corresponding cyclopropanes or to release of a carbene species. The formation of a pyrazole via [3+2]-cycloaddition (32CA) is observed only in reactions with (trimethylsilyl)diazomethane, which behaves similar to the parent diazomethane. The proposed mechanisms were analyzed computationally using the DFT method.

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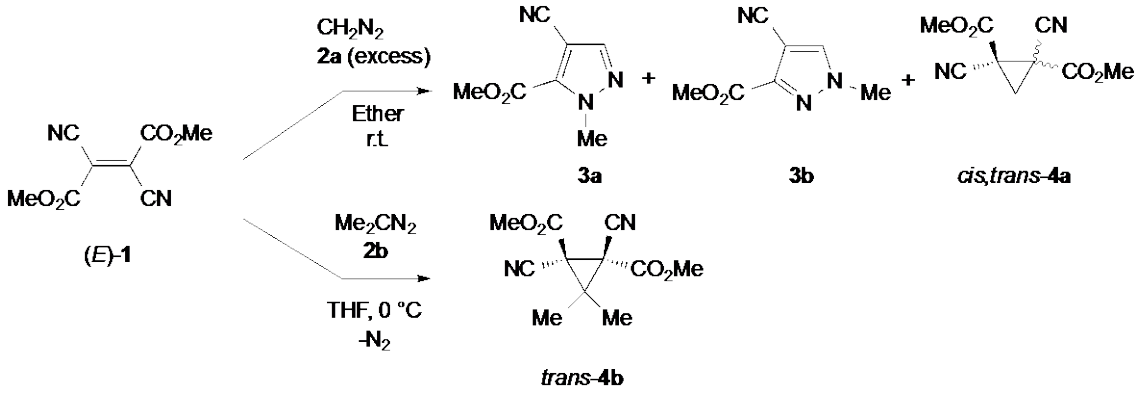
Keywords Diaryldiazomethanes, dicyanobutenedioates, (trimethylsilyl)diazomethane, reaction mechanism, cyclopropanation, DFT calculations

Introduction

The [3+2]-cycloadditions (32CA) of activated ethenes with diazomethanes as three atom components (TACs) constitute an important method for the formation of pyrazolines.[1,2] In the presence of a metal catalyst or under photolytical conditions, the initial decomposition of the diazo compounds leads to a reactive carbenoid or carbene, respectively, which reacts with the C=C bond to give the corresponding cyclopropane derivative.[3a] In a recent publication, efficient cyclopropanations of some electron deficient ethenes using unstable aryl diazomethanes generated under 'continous flow conditions' were described.[3b] An attractive, photocatalytical approach based on the usage of the blue-led light, which has extensively been developed in recent years,[3c] was also successfully applied for cyclopropanation rections of some electron rich ethylenes using diversely substituted alkyl diazoarylacetates.[3d] These formal [2+1]-cycloadditions occur stereoselectively or non-stereoselectively depending on the properties of the reactive intermediate.

In a series of recent studies, electron-deficient dimethyl (*E*)- and (*Z*)-2,3-dicyanobutenedioates **1** (dicyanofumarate (*E*)-**1** and dicyanomaleate (*Z*)-**1**) were described as superior components of 32CAs with TACs such as thiocarbonyl *S*-methanides, azomethine ylides, and diazoalkanes.[4] Whereas the reaction with diazomethane (**2a**) afforded mixtures of pyrazole derivatives and stereoisomeric cyclopropanes,[5] reactions with 2-diazopropane (**2b**) led to exclusive formation of the corresponding cyclopropanes in a stereoselective manner[6] (Scheme 1).



Scheme 1. Reactions of diazoalkanes **2a**,**b** with dimethyl dicyanofumarate ((*E*)-**1**) (ref. [5-6]).

9-Diazofluorene (**2c**) and diphenyldiazomethane (**2d**) are easily available and both compounds are widely applied in reactions with diverse ethylene derivatives. For example, in a recent publication, attempted 32CAs of **2c** with 2-aryl-1-cyano-1-nitroethylenes were described. Unexpectedly, instead of pyrazoles, 2,3-diazabuta-1,3-dienes were obtained and identified by X-ray crystallography.[7] The formation of these products was explained by the appearance of a zwitterionic intermediate, which after extrusion of cyano(nitro)carbene converted into the final product. On the other hand, both **2c** and **2d** were applied for the [3+2]-cycloaddition with an electron-deficient acetylene and the corresponding pyrazoles were obtained regioselectively in good yields.[8] In contrast to **2c** and **2d**, bis(4-methoxyphenyl)diazomethane (**2e**), 5-diazo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (**2f**), and 5-diazo-5*H*-dibenzo[*a*,*d*]-cycloheptene (**2g**) are rarely applied in cycloaddition reactions, and cyclopropanations with **2e**–**g** have not been reported yet.

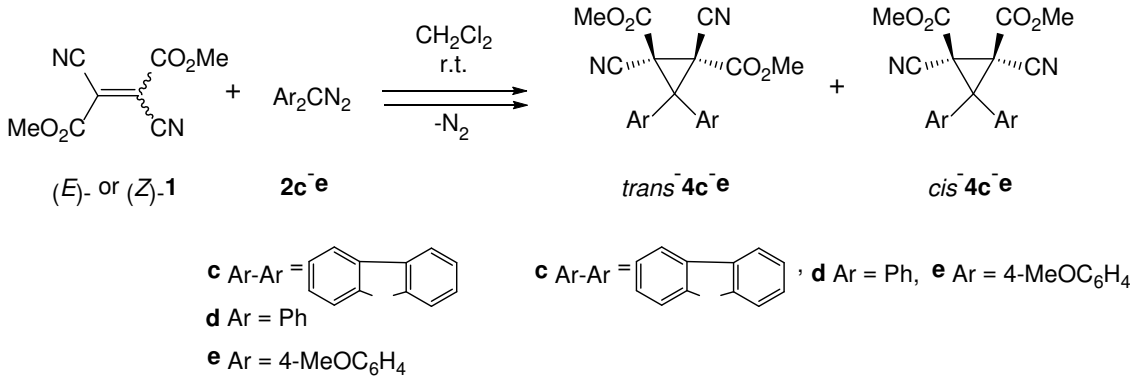
In a recent publication, Domingo et al. explained the reaction of 1-diazopropan-2-one with 1,1-dinitroethylene,[9] which leads to a mixture of 2-actyl-1,1-dinitrocyclopropane and 3-acetyl-5-nitropyrazole,[10] on the basis of the Molecular Electron Density Theory (MEDT).[11] According to these studies, the formations of both the cyclopropane derivative and the pyrazole occur via domino reactions with the initial formation of 5-acetyl-3,3-dinitro-4,5-dihydro-3*H*-pyrazole in a [3+2]-cycloaddition (32CA).

In the present report, the reactions of (*E*)-**1** and (*Z*)-**1** with diaryldiazomethanes **2c**–**g** will be described and the observed reaction courses will be compared with that

obtained with (trimethylsilyl)diazomethane (**2h**). The experimental results will be supplemented with computational studies aimed at the elucidation of the reaction mechanisms.

Results and discussion

The first two experiments were performed with (*E*)- and (*Z*)-**1** and bis(4-methoxyphenyl)diazomethane (**2e**) in CH_2Cl_2 solution at room temperature. The initially blue-colored reaction mixture decolorized immediately and a vigorous evolution of N_2 was observed in both cases. The ^{1}H NMR analyses of the crude reaction mixtures showed identical compositions of products in both experiments. Chromatographic separation led to two isomeric products. The major one, obtained as the more polar fraction, was identified as dimethyl *trans*-1,2-dicyano-3,3-bis(4-methoxyphenyl)cyclopropane-1,2-dicarboxylate (*trans*-**4e**, Scheme 2). The configuration of this isomer was confirmed by the presence of two singlets at 3.73 and 3.84 ppm, each for two MeO groups. In the ^{13}C NMR spectrum, only one signal for C≡N (112.2 ppm) and one signal for **C**O_2Me (161.2 ppm) was present. The ^{1}HNMR spectrum of the minor, less polar *cis*-isomer showed three singlets at 3.71, 3.75, and 3.84 ppm for MeO groups in a ration of 1:1:2. The first two signals are attributed to $MeOC_6H_4$ groups and the last signal originates from two equivalent methyl ester groups. The chemical shifts of the pure isomers allowed the determination of the ratio of *trans*- and *cis*-**4e** in the crude reaction mixture to ca. 1.6:1.



Scheme 2. Cyclopropanation reactions of (*E*)- and (*Z*)-**1** with diaryldiazomethanes **2c**–**e**.

The next experiment was carried out using (*E*)-**1** and **2c** in CH_2Cl_2 solution at room temperature using the substrates in a 1:1 molar ratio. The progress of the reaction was monitored by TLC and, after 2 h, no **2c** could be detected in the mixture. However, the ^{1}H NMR spectrum indicated that a substantial amount of (*E*)-**1** was still present. Apparently, **2c** was partially converted into the known orange bisfluorenylidene. For that reason, the experiment was repeated using (*E*)-**1** and **2c** in a 1:3 ratio. In that case, the ^{1}H NMR spectrum of the crude mixture after 2 h showed complete conversion of (*E*)-**1**, and two singlets for MeO groups found at 3.83 and 3.90 ppm revealed the presence of two products in a ratio of ca. 3:1. The undesired bisfluorenylidene was removed by trituration with CH_2Cl_2 and the mother liquor, after evaporation of the solvent, afforded a solid, which after crystallization gave the major product as a crystalline material with m.p. 237–239 ºC. The ^{1}H NMR spectrum showed a singlet at 3.83 ppm for two MeO groups and a set of four multiplets characteristic for the fluorene moiety. The ^{13}C NMR spectrum confirmed the structure of a dimethyl 1,2-dicyanocyclopropane-1,2-dicarboxylate. The expected *trans*-configuration of this product, *trans*-**4c** (Scheme 2), was unambiguously established by X-ray crystallography (Figure 1).

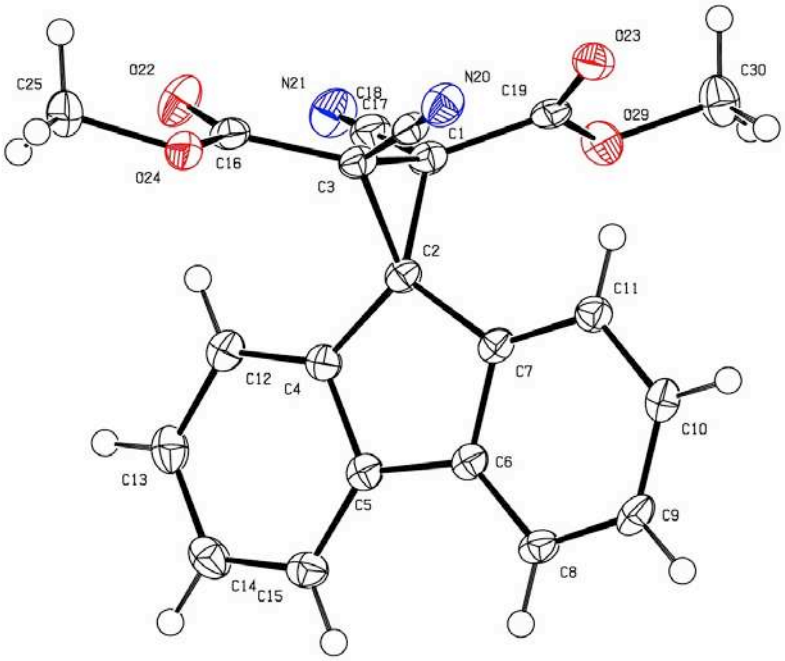


Figure 1. A view of the molecular structure of compound *trans*-**4c**. Displacement ellipsoids are drawn at the 50% probability level. X-ray data collected at 100 K.

The mother liquor after crystallization of *trans*-**4c** was concentrated and the semi-solid residue was subjected to preparative layer chromatography. The less polar fraction formed colorless crystals with m.p. 222−224 ºC, which were identified, based on spectroscopic data, as *cis*-**4c**, contaminated with an unknown product.

In a supplementary control experiment, **2c** was reacted with (*Z*)-**1**, and in that case, complete consumption of the less reactive (*Z*)-**1** was achieved only after 24 h. The two isomeric products *trans*- and *cis*-**4c** were present in the crude mixture in a ratio of ca. 1:1 (^{1}H NMR). It is worth mentioning that almost the same ratio was found in a control spectrum registered after 2 h of the experiment, and only (*Z*)-**1** was detected in this spectrum.

Diphenyldiazomethane (**2d**) behaves differently in reactions with (*E*)- and (*Z*)-**1**. The reaction with (*E*)-**1**, performed according to the protocol described for **2c**, required 24 h to be complete. The ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of one major product with a characteristic singlet for MeO at 3.84 ppm. Careful analysis of the ^{1}H NMR spectrum of the crude mixture allows estimating the presence of the minor cyclopropane and the ratio of both diastereoisomers to ca. 9:1. After evaporation of the solvent, the residue was crystallized from methanol yielding a colorless crystalline product. The tentatively proposed structure *trans*-**4d** was elucidated by comparison of the NMR data with those of *trans*-**4c**. For example, the ^{13}C signal for two C≡N groups in *trans*-**4c** is located at 111.0 ppm and in *trans*-**4d** at 112.0 ppm. In addition, the signals for the CO_2Me groups appear at 160.0/54.8 and 161.1/54.6 ppm, respectively. In addition, the *trans*-configuration of this isomer was confirmed by the appearance of only one signal for an aromatic C atom (135.2 ppm) and three signals of non-equivalent, aromatic CH-units at 129.6, 129.3, and 127.9 ppm.

The reaction of (*Z*)-**1** with **2d** was much faster and complete decolorization of the diazo compound was observed after 3 h. The ^{1}H NMR spectrum of the crude mixture allowed establishing the presence of the major cyclopropane *cis*-**4d**, accompanied by a small admixture of the above-described *trans*-**4d** in a ratio of ca. 90:10. The chromatographic separation of the 'cyclopropane fraction' followed by fractional crystallization allowed to isolate pure *cis*-**4d**. In that case, its configuration

was unambiguously confirmed by the appearance of two signals for aromatic C atoms (136.6 and 133.4 ppm) and six CH-signals for two non-equivalent aromatic rings.

In comparison with **2c**–**e**, the reactivities of **2f** and **2g** towards (*E*)- and (*Z*)-**1** differ dramatically. Whereas in the reaction of (*E*)-**1** with **2f** the blue color of the solution vanished after 4 h, the analogous experiment with **2g** required 72 h. In both cases, after decolorization of the reaction solutions, the ^{1}H NMR spectra of the crude mixtures evidenced the presence of the non-converted (*E*)-**1**. After workup, in each case a colorless solid was isolated, and the spectroscopic data, supported by elemental analyses, allowed to identify them as ethylene **5**[12] and azine **6**,[13] respectively (Figure 2). Whereas compound **5** can be considered as the dimer of the carbene generated from **2f**, product **6** may result from the reaction of the *in situ*-generated analogous carbene with its precursor, i.e. **2g**. The same products were formed in reactions of (*Z*)-**1** with **2f** and **2g**, respectively.

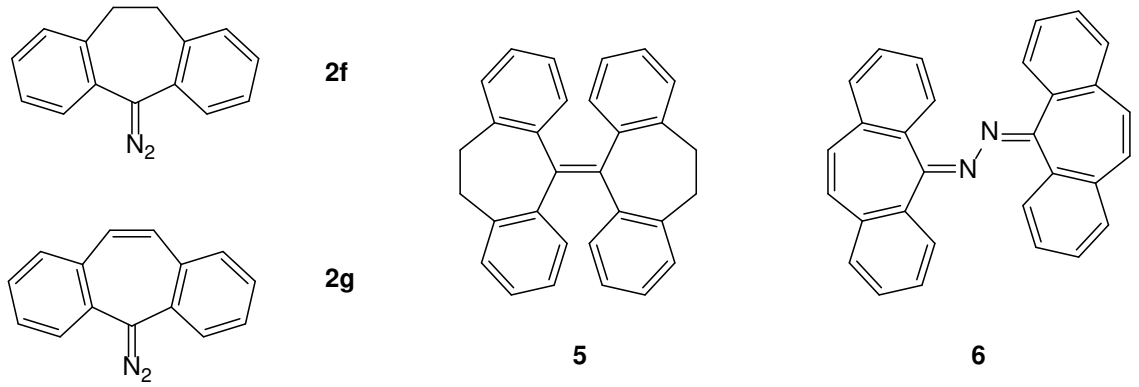
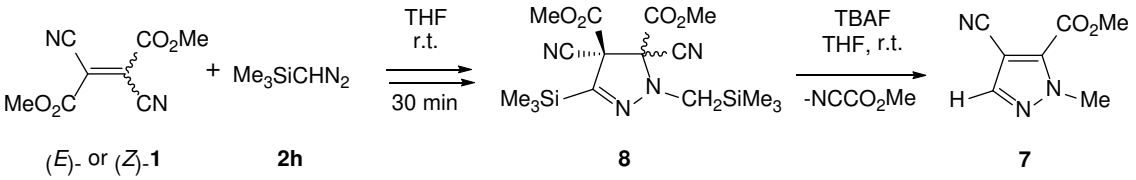


Figure 2. Products **5** and **6** obtained in reactions of (*E*)-**1** with diazocompounds **2f** and **2g**, respectively.

In extension of the study and in order to compare the reaction courses of (*E*)-**1** with diazomethane (**2a**)[5] and diaryldiazomethanes **2c**–**e**, (trimethylsilyl)diazomethane (**2h**) was also tested. The experiment with (*E*)-**1** and a two-fold excess of **2h** was performed in THF at room temperature. After 30 min, tetrabutylammonium fluoride (TBAF) was added to remove the TMS group from the products formed. The crude reaction mixture was separated by column chromatography, which afforded only one product isolated as a crystalline material. The ^{1}H NMR spectrum showed three signals located at 4.00, 4.22 and 7.79 ppm with an intensity ratio of 3:3:2. The ^{13}C NMR

spectrum suggested the presence of only one ester group by the signal at 158.1 ppm. These data did neither correspond with the expected structures of a pyrazoline derivative nor with that of cyclopropane derivatives. Finally, the structure of this product was determined by X-ray crystallography (Fig. 3), which showed that the compound was identical with the already reported methyl 4-cyano-1-methylpyrazole-5-carboxylate (**7**, Scheme 3).[5,14] The analogous experiment performed with (*Z*)-**1** led to the same product. Elimination of methyl cyanoformate from the dimethyl pyrazole dicarboxylate analogous to **8**, obtained after [3+2]-cycloaddition of (*E*)-**1** with the parent diazomethane, which also led to product **7**, was carefully studied by Huisgen.[5a]



Scheme 3. Reaction sequence via [3+2]-cycloaddition, desilylation and elimination leading to pyrazole **7**.

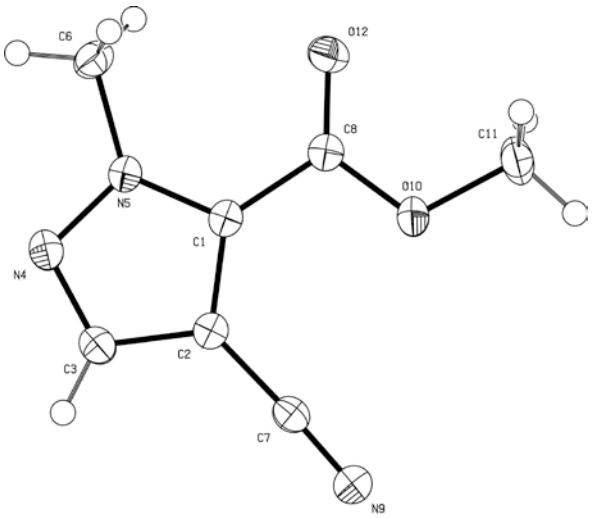
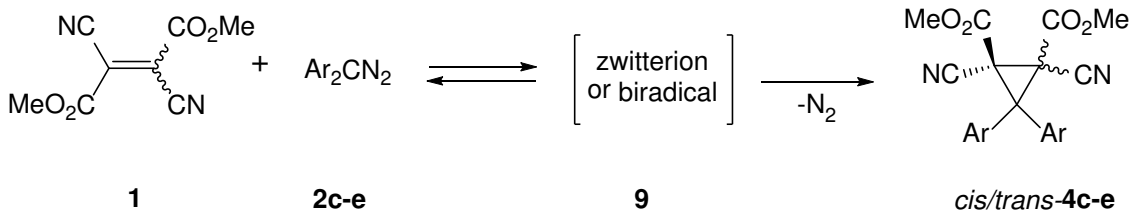


Figure 3. A view of the molecular structure of compound **7**. Displacement ellipsoids are drawn at the 50% probability level. X-ray data collected at 100 K.

The reported reactions of 9-diazofluorene (**2c**) and diphenyldiazomethane (**2d**) with the electron-deficient tetracyanoethylene (TCNE) offer a straightforward access to the corresponding cyclopropanes.[15,16] The supposed mechanism for their formation

involves the initial [3+2]-cycloaddition leading to pyrazolines, which upon heating were converted into cyclopropanes via N_2 elimination. The same mechanism was believed to occur in reactions aimed at the determination of reaction rates.[17,18] In the present study, the use of the isomeric ethylene derivatives (*E*)-**1** and (*Z*)-**1** in reactions with **2c**–**e** allows getting more information about the reaction mechanism. Despite the fact that the reactions were performed under mild conditions, a spontaneous evolution of N_2 was observed. Moreover, the ^{1}H NMR control evidenced the presence of cyclopropanes **4** as the only products over the entire reaction time. Based on these observations and loss of the stereochemical integrity, we postulate that these reactions follow a stepwise zwitterionic or diradical mechanism (Scheme 4).



Scheme 4. Proposed, stepwise reaction mechanism for the formation of cyclopropanes **5**.

In order to obtain an additional support for the proposed molecular mechanism of the formation of stereoisomeric cyclopropanes in reactions of (*E*)-**1** and (*Z*)-**1** with **2c**–**e**, theoretical DFT studies were performed. Firstly, we analyzed global and local conceptual DFT reactivity indices of the reagents. It is generally known[19] that 32CAs require nucleophilic activation of the molecule of one of the addends, and electrophilic activation of the second component, in order to favor the reaction through a polar process.[20] This type of activation is also observed in the series of reactions between **1** and diaryldiazomethanes **2c**−**e**. In particular, (*E*)-**1** is characterized by high global electrophilicity, in excess of 4 eV. For the same molecule the global nucleophilicity index was calculated to the value of only 1.03 eV. Therefore, it should be classified to the group of strong electrophiles within the reactivity scale proposed by Domingo.[21] On the other hand, calculated global electrophilicities of diaryldiazomethanes 2c−e are in the range of 1.30−1.84 eV, whereas global nucleophilicities are in excess of 3.5 eV (Table 1). Based on these data, one can assume that the initial step of theses reactions is

the interaction between one of the equivalent C=C atoms of (*E*)-**1** and the more nucleophilic, activated centre of the diazo compound. The analysis of the local reactivity in molecules **2c**−**e** shows clearly that the more active center is located on the terminal nitrogen atom of the diazo function. In consequence, the analyzed process will be initiated by the attack of this atom onto the C=C bond of (*E*)-**1**. Analogous distribution of local reactivity can be interpreted for the reaction of (*Z*)-**1** with **2c**−**e**.

Table 1. Global and local electronic properties for diazomethanes **2c**−**g**.

	Global properties				Local properties			
	μ [eV]	η [eV]	ω [eV]	N [eV]	P^-_C	P^-_N	N_C [eV]	N_N [eV]
2c	−3.67	3.67	1.84	3.61	0.23	0.39	0.83	1.41
2d	−3.36	3.70	1.52	3.91	0.23	0.41	0.91	1.62
2e	−3.02	3.52	1.30	4.34	0.15	0.38	0.64	1.65
2f	−3.33	3.69	1.51	3.94	0.24	0.40	0.93	1.57
2g	−3.36	3.41	1.65	4.06	0.17	0.34	0.68	1.39
(*E*)-**1**	–5.96	4.27	4.16	1.03				
(*Z*)-**1**	–5.85	4.58	3.73	0.98				

Next, the detailed possible pathways of transformations of the addends were analyzed. This study was performed for the model process (*E*)-**1**+**2c**. The DFT calculation showed that the formations of isomeric cyclopropanes **4c** proceed following a multi-step mechanism presented in Scheme 4 and Fig. 4.

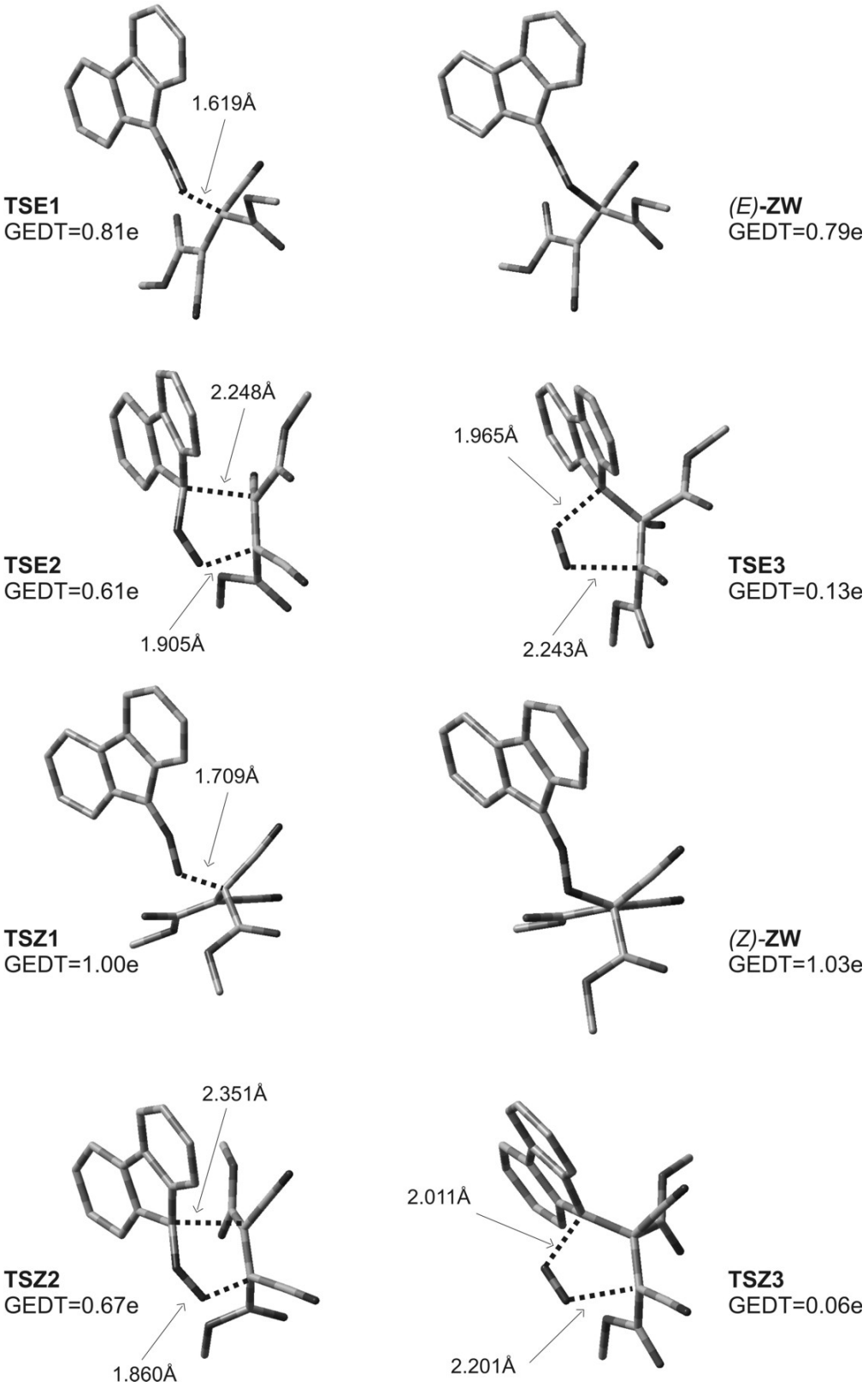


Figure 4. Views of key critical structures for reactions **1**+**2c** according to B3LYP/6-31++G(d)(PCM) computational study

In particular, the conversion of the reaction system (*E*)-**1**+**2c** into *trans*-**4c** is a domino process, occurring via a labile 5-membered heterocyclic intermediate, a 4,5-dihydro-3*H*-pyrazole (**32CA**, Scheme 5), which might be considered as a formal [3+2]-cycloadduct. The first step of this conversion (path **A** in Scheme 5) requires a Gibbs free energy of activation calculated to 35.5 kcal/mol and leads to cycloadduct *trans*-**32CA**, which is evidently unstable from the thermodynamic point of view. Therefore, two competitive transformations of this intermediate are possible: (a) a [3+2]-cycloelimination (cycloreversion) reaction leading to **2c** and (*E*)-**1**; (b) irreversible nitrogen extrusion (path **B** in Scheme 5), which proceeds via a single transition state, yielding *trans*-**4c**. Both processes proceed via 5-membered transition states (**TSE2** and **TSE3**, respectively), the nature of which was confirmed by vibrational analysis and IRC calculations. It is worth mentioning that the nitrogen extrusion from pyrazoline ring requires rather high energy of activation (Figure 5). This interpretation would require a diastereoselective course of the analyzed reaction. However, the performed experiments led to the formation of two isomeric cyclopropanes *cis*- and *trans*-**4c**. For this reason, a competitive mechanism for the conversion of the addends should be considered. In particular, primary interaction in the reaction system (*E*)-**1**+**2c** may lead via transition state **TSE1** to the intermediate (*E*)-**ZW** (path **C** in Scheme 5), whose zwitterionic nature was confirmed by the GEDT analysis (Fig. 5).

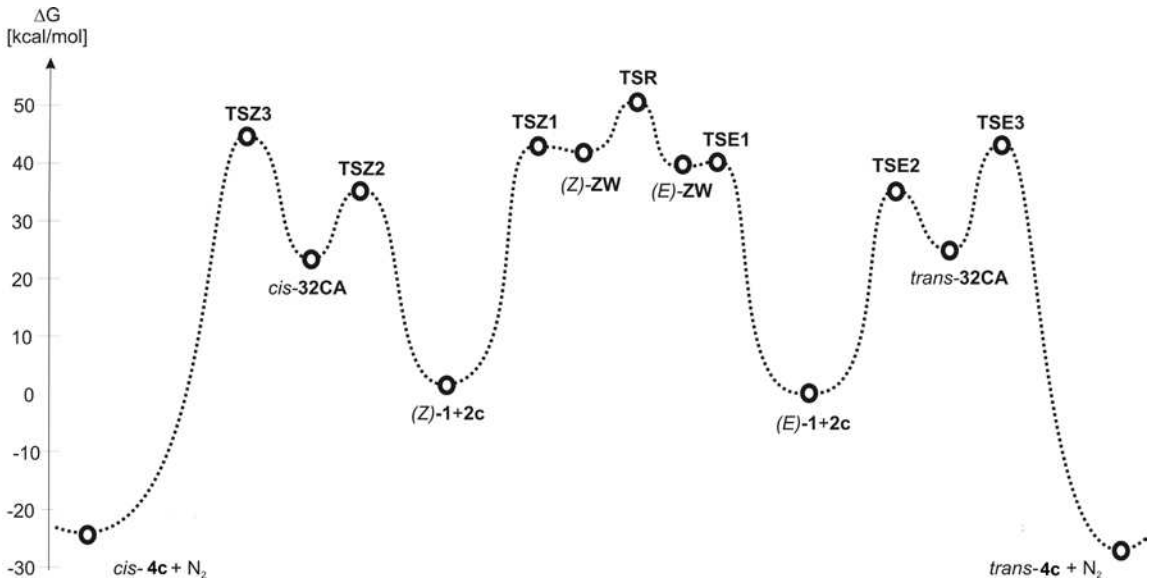
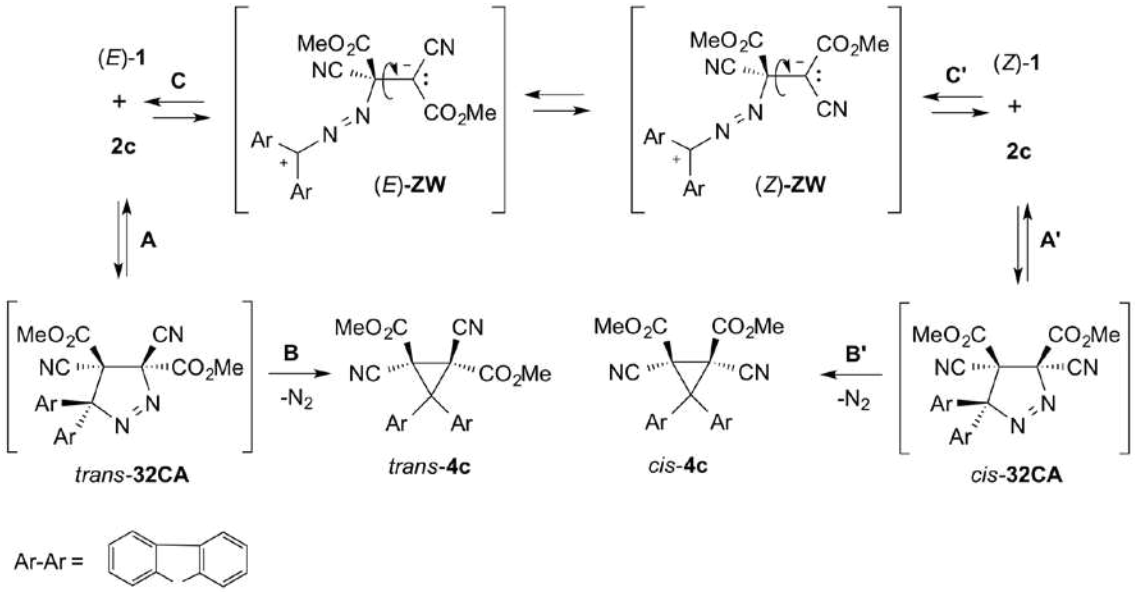


Figure 5. Gibbs free energy profiles for the reaction (*E*)-**1**+**2c** according to B3LYP/6-31++G(d)(PCM) computational study

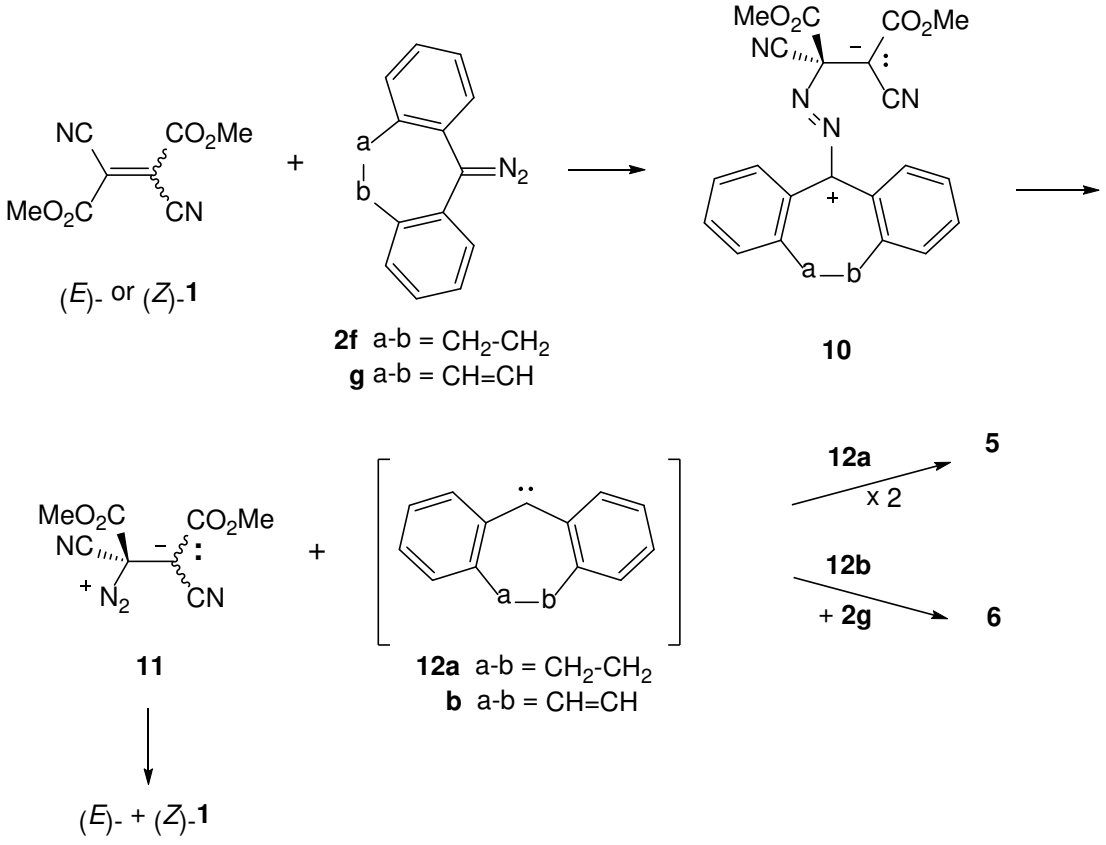
The (*E*)-**ZW** is characterized by an 'extended' conformation, which can't undergo the ring closure. A similar type of intermediate was identified recently on the basis of comprehensive theoretical and experimental studies for the reaction between **2c** and 2-phenyl-1-cyano-1-nitroethene.[7] In these types of zwitterionic intermediates, rotation around the C–C bond in the ethylene derivative substructure is likely and was confirmed experimentally in reactions performed with electron-rich thiocarbonyl *S*-methanides and both isomers of **1**.[22] Consequently, the isomeric (*Z*)-**ZW** zwitterion is formed and its dissociation leads to a mixture of (*Z*)-**1** and **2c**, which may further be converted into *cis*-**4c** via **TSZ2** and **TSZ3** in analogy to the transformation (*E*)-**1**+**2c**→*trans*-**4c**. Thus, the performed DFT study fully explained the domino mechanism of the studied reactions leading to mixtures of diastereoisomeric cyclopropanes starting with (*E*)-**1** or (*Z*)-**1** as the required electron deficient ethylene derivative. This mechanism is outlined in Scheme 5.



Scheme 5. Domino reaction mechanism for the formation of cyclopropanes **4c** in the light of B3LYP/6-31++G(d)(PCM) computational study.

The stepwise mechanism with the initial attack of the N-terminus of diazofluorene (**2c**) onto the activated C=C bond with subsequent elimination of a carbene species leads to the formation of 2,3-diaza-1,3-butadienes has been described in ref. [7]. The same interpretation can be applied to explain the results obtained with **2f** and **2g**. In particular, analysis of local nucleophilicities suggests that reactions are

initiated by the analogous attack of the more nucleophilic, terminal nitrogen atom of the diazo fragment (Table 1). This type of the attack leads to the formation of the reactive intermediates of type **10** (Scheme 6). However in these cases, the intermediates **10** undergo dissoziation leading to betaines **11** and carbenes **12** with no competitive conversion leading to cyclopropanes via 5-membered heterocyclic intermediates. The latter intermediates, depending on the structure and, therefore, on the reactivity of the diazo compound **2**, undergo either dimerization yielding ethene **5** or addition onto the less reactive diazo group of the less reactive **2g** to give azine **6**. The betaine **11** most likely eliminates spontaneously N_2 releasing the starting ethylene derivative **1**. Formally, the formation of **11** can be understood as an in-situ diazo-transfer reaction.



Scheme 6. Proposed reaction mechanism for the formation of carbenes **12**, ethane **5** and azine **6**.

The presented explanation can also be applied for the reaction course observed in the case of diazofluorene (**2c**). Apparently, this diazo compound reacts with **1** via two

competitive reaction pathways, and both a C–C and a C–N bond are formed in the initial step, leading finally to cyclopropanes **4c** and to bisfluorenylidene, respectively.

The comparison with the results obtained with diazomethanes **2c**–**g** shows that diaryldiazomethanes **2c**–**e** and **2f**,**g** react with **1** via stepwise mechanisms but the structure of the final products depends on the type of TACs used in the reaction. An alternative SET (single electron transfer)-mechanism initiated by the electron transfer from the electron-rich diazo compound to the electron-deficient ethylene acceptor should be also considered, but the products formed via the in situ generated carbene support the presented zwitterionic or diradical interpretation.

A plausible reaction mechanism leading to **7**, obtained in a rather low yield from the reaction of **2h** with (*E*)- and (*Z*)-**1** followed by desilylation is formulated in Scheme 3. In that case, in contrast to diaryldiazomethanes, the initial step comprises the [3+2]-cycloaddition leading to the five-membered cycloadduct, which after 1,3-H shift and 'methylation' with **2h** forms the intermediate **8**. The latter, without isolation, is converted into **7** via desilylation and elimination of methyl cyanoformate. The same product was reported for the reaction of excess **2a** and (*E*)-**1** in ethereal solution (Scheme 1), and its formation was explained based on a similar mechanistic interpretation.[5]

It is worth mentioning that the reactions of **2h** with tetracyanoethylene and other electron-deficient ethenes lead to the corresponding cyclopropanes, and no pyrazole derivatives were reported.[23] Unfortunately, no experimental data are available in this publication. Nevertheless, based on our results, a similar, stepwise mechanism can be formulated for all presented cases related to the synthesis of cyclopropanes in reactions with strongly electron deficient teracyanethylene.

3. Conclusions

The preparation of cyclopropanes with electron-withdrawing substituents is of current interest[13,24,25], and the most frequently applied methods for their synthesis are metal-catalyzed or metal-free reactions of diazo compounds with electron-deficient alkenes. The present study showed that the reactions of both dimethyl dicyanofumarate (*E*)-**1** and dicyanomaleate (*Z*)-**1** with diazomethanes **2** lead to different products depending on the type of the used diazo compound. Apparently, these reactions take place via domino processes, which are initialized by a 32CA reaction between the aryldiazomethane and

the electrophilic ethylene, yielding the corresponding 1-pyrazoline. The subsequent reactions, which determine the type of the final products, depend on both electronic and steric factors. Whereas diphenyldiazomethanes **2c**–**e** afford mixtures of isomeric cyclopropanes exclusively, the sterically crowded diazo compounds **2f**–**g** react with **1** to give products resulting from the intermediacy of the in situ generated cyclic carbenes. Thus, in the reaction with the more reactive **2f**, the dimer **5** was obtained, but in the case of the very slow reaction with **2g**, the extruded carbene species reacts with the diazo precursor present in the reaction mixture forming the azine **6**. The postulated domino reactions of diazo compounds **2c**–**e** with electron deficient, *E*/*Z*-isomeric ethylenes **1** are supported by DFT calculations. On the other hand, (trimethylsilyl)diazomethane (**2h**), in analogy to the parent diazomethane (**2a**)[5] reacts with **1** via [3+2]-cycloaddition leading to five-membered pyrazole derivatives, which in the case of the silylated [3+2]-cycloadduct undergoes further conversions upon treatment with TBAF solution. In both cases, elimination of methyl cyanoformate from the initially formed pyrazole dicarboxylate was observed.

Experimental Section

General: All solvents were dried over appropriate drying agents and distilled before use. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, respectively), using the solvent ($CDCl_3$, residual $CHCl_3$) signal as reference. The following abbreviations are used to describe peak patterns where appropriate: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), dd (doublet × doublet), and td (triplet × doublet). Coupling constants (*J*) are reported in Hertz (Hz). The IR spectra (KBr pellets) were recorded on a Nexus FT-IR spectrophotometer. The elemental analyses were determined on a Vario Micro Cube. Flash column chromatography (FCC) was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). Melting points were determined in a capillary using a Stewart® SMP30 apparatus.

Starting materials: (*E*)- and (*Z*)-Dimethyl dicyanofumarates ((*E*)-**1** and (*Z*)-**1**) were obtained according to published procedures starting with methyl dicyanoacetate and HCl-free thionyl chloride.[26] Bis(4-methoxyphenyl)diazomethane (**2e**),[27] diphenyldiazomethane (**2d**),[28] 9-diazofluorene (**2c**),[28] 5-diazo-10,11-dihydro-5*H*-

dibenzo[a,d]cycloheptene (**2f**),[28] and 5-diazo-5*H*-dibenzo[a,d]cycloheptene (**2g**),[28] were prepared from the corresponding hydrazones by oxidation with activated manganese dioxide (MnO_2)[27] or with yellow mercury oxide (HgO).[29] Hydrazones of bis(4-methoxyphenyl)ketone, 9*H*-fluorenone, and 10,11-dihydro-5*H*-dibenzo[a,d]cycloheptenone were efficiently prepared from the corresponding thioketones[30] by treatment with hydrazine hydrate in ethanolic solutions; all reactions were completed after 10–30 min at room temperature and the required hydrazones were obtained in 80–90% yield. Trimethysilyl diazomethane (**2h**) and other reagents used in the study were commercially available substances.

Reactions of diaryldiazomethanes 2 with (*E*)- or (*Z*)-dimethyl dicyanofumarates 1. General procedure: A solution of 194 mg (1 mmol) of **1** and 3 mmol of the respective **2** in 2 mL of dichloromethane was stirred magnetically at room temperature until the characteristic violet color of the starting diazo compound vanished. Only in the case of **2c**, the fast reaction with (*Z*)-**1** was completed after 30 min using only 1.2 mmol of the diazo compound. After evaporation of the solvent, crude mixtures were analyzed by ^{1}H NMR spectroscopy and subsequently separated chromatographically on plates coated with silica gel (PLC). Typically, a mixture of petroleum ether and ethyl acetate (4:1) was used as an eluent. The isolated 'cyclopropane fraction' with R_f ca. 0.5 was additionally separated either by repeated chromatography or by fractional crystallization. The ratios of isomeric *trans*- and *cis*-cyclopropanes **4c**–**e** formed in experiments with diaryl diazomethanes **2c**–**e** were determined based on the ^{1}H NMR analysis of the initially isolated 'cyclopropane fractions'. After separation, analytically pure samples were obtained by crystallization.

Reaction with Bis(4-methoxyphenyl)diazomethane (**2e**): Experiment A: molar ratio (*E*)-**1/2e** = 1:1.2; reaction time: 30 min; *trans*-**4e** : *cis*-**4e** = ca. 85:15. Experiment B: molar ratio (*Z*)-**1/2e** = 1:1.2; reaction time: 20 min; *trans*-**4e** : *cis*-**4e** = ca. 60:40.

***trans*-Dimethyl 1,2-Dicyano-3,3-bis(4-methoxyphenyl)cyclopropane-1,2-dicarboxylate** (*trans*-**4e**): Less polar fraction, colorless crystals, m.p. 178–179 °C (from MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37, 6.84 (2d, $J_{H,H}$ = 6.0 Hz, 8 arom. CH), 3.84, 3.73 (2s, 6 H, 2 OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.2 (2 C=O), 159.7 (2 arom. C), 128.6, 114.8 (8 arom. CH), 127.5 (2 arom. C), 112.2 (2 CN), 55.5,

54.6 (2 OCH_3), 52.6, 36.3 (2 C) ppm. IR (KBr): υ = 2962 (w), 2837 (w), 2252 (C≡N), 1752 (vs, C=O), 1609 (m), 1513 (s), 1466 and 1436 (m), 1247 (vs., br. O–C), 1026 (s), 889 (m), 838 (m), 582 and 571 (m) cm^{-1}. EA for $C_{23}H_{20}N_2O_6$ (420.41): calcd. C 65.71, H 4.79, N 6.66; found C 65.5, H 4.80, N 6.69.

***cis*-Dimethyl 1,2-Dicyano-3,3-bis(4-methoxyphenyl)cyclopropane-1,2-dicarboxylate** (*cis*-**4e**): Colorless crystals, m.p. 108–111 °C (from MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48, 6.90 (2d, $J_{H,H}$ = 6.0 Hz, 4 arom. CH), 7.33, 6.76 (2d, $J_{H,H}$ = 6.0 Hz, 4 arom. CH), 3.84 (s, 6 H, 2 OCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 160.9 (2 OCH_3), 159.9, 159.3 (2 arom. C), 129.6, 129.2, 114.9, 113.9 (8 arom. CH), 129.1, 125.7 (2 arom. C), 113.2 (2 CN), 55.2, 55.1 (2 OCH_3), 54.4 (2 OCH_3-ester), 53.9 (C), 37.2 (2 C) ppm. IR (KBr): υ = 2837 (w), 2248 (w), 1759 (vs, C=O), 1609 (m), 1514 (vs), 1458 and 1437 (m), 1254 (vs, br, O–C), 1176 (m), 1149 (m), 1035 (s), 910 (m), 843 (m), 592 (m), 568 (m) cm^{-1}. EA for $C_{23}H_{20}N_2O_6$ (420.41): calcd. C 65.71, H 4.79, N 6.66; found C 65.57, H 4.92, N 6.70.

Reaction with 9-Diazofluorene (**2c**): Experiment A: molar ratio (*E*)-**1/2c** = 1:3; reaction time: 24 h; *trans*-**4c** : *cis*-**4c** = ca. 65:35. Experiment B: molar ratio (*Z*)-**1/2c** = 1:3; reaction time: 3 h; *trans*-**4c** : *cis*-**4c** = ca. 74:26.

***trans*-Dimethyl 2,3-Dicyanospiro[cyclopropane-1,9'-fluorene]-2,3-dicarboxylate** (*trans*-**4c**): Colorless crystals, m.p. 236–238 °C (from MeOH)). ^{1}H NMR ($CDCl_3$): δ = 7.84–7.35 (4m, 8 arom. CH), 3.83 (s, 6 H, 2 OCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.0 (2 C=O), 141.7, 134.4 (4 arom. C), 130.4, 128.0, 123.8, 120.7 (8 arom. CH), 111.0 (2 CN), 54.8 (2 OCH_3), 45.0 (C), 34.9 (2 C) ppm. IR (KBr): υ = 2246 (w, C≡N), 1755 (vs, C=O), 1454 (m), 1249 (s, O–C), 742 (m), 653 (w) cm^{-1}. EA for $C_{21}H_{14}N_2O_4$ (358.35): calcd. C 70.39, H 3.94, N 7.82; found C 70.44, H 4.01, N 7.82.

***cis*-Dimethyl 2,3-Dicyanospiro[cyclopropane-1,9'-fluorene]-2,3-dicarboxylate** (*cis*-**4c**): Colorless crystals, m.p. 222–224 °C (from MeOH). ^{1}H NMR ($CDCl_3$): δ = 7.99–7.25 (5m, 8 arom. CH), 3.90 (s, 6 H, 2 OCH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 159.7 (2 C=O), 142.4, 141.2, 134.8, 132.7 (4 arom. C), 130.4, 130.1, 127.9, 127.1, 125.1, 120.2, 120.22, 120.17 (8 arom. CH), 111.9 (2 CN), 54.6 (2 OCH_3), 47.1 (C), 35.8 (2C) ppm. IR (KBr): υ = 2955 (w), 2243 (C≡N), 1767 and 1750 (vs, C=O), 1452 and 1433 (s),

1274 and 1244 (vs, br. O–C), 1147 (m), 1087 (w), 936 (w), 900 (w), 733 (vs), 653 (m) cm^{-1}. EA for $C_{21}H_{14}N_2O_4$ (358.35): calcd. C 70.39, H 3.94, N 7.82; found C 70.26, H 3.91, N 7.73.

Reaction with Diphenyldiazomethane (**2d**): Experiment A: molar ratio (*E*)-**1**/**2d** = 1:3; reaction time: 24 h; *trans*-**4d** : *cis*-**4d** = 57:43. Experiment B: molar ratio (*Z*)-**1**/**2d** = 1:3; reaction time: 3 h; *trans*-**4d** : *cis*-**4d** = 55:45.

***trans*-Dimethyl 1,2-Dicyano-3,3-diphenylcyclopropane-1,2-dicarboxylate** (*trans*-**4d**): Colorless crystals, m.p. 221–223 °C (from MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50–7.26 (3m, 10 arom. CH), 3.84 (s, 6 H, 2 OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 161.2 (2 C=O), 135.2 (2 arom. C), 129.6, 129.3, 127.9 (10 arom. CH), 112.1 (2 CN), 54.8 (2 OCH_3), 53.5 (C), 36.1 (2 C) ppm. IR (KBr) υ = 2255 (w, C≡N), 1761 and 1746 (vs, C=O), 1496 (m), 1454 and 1429 (m), 1306 (m), 1233 (vs, O–C), 1106 (m), 945 (w), 884 (w), 751 (m), 707 (s), 578 (m) cm^{-1}. EA for $C_{21}H_{16}N_2O_4$ (360.36): calcd. C 69.99, H 4.47, N 7.77; found C 70.27, H 4.54, N 7.50.

***cis*-Dimethyl 1,2-Dicyano-3,3-diphenylcyclopropane-1,2-dicarboxylate** (*cis*-**4d**): Colorless crystals, m.p. 146–148 °C (from MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62–7.20 (6m, 10 arom. CH), 3.83 (s, 6 H, 2 OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.8 (2 C=O), 136.6, 133.4 (2 arom. C), 129.5, 129.3, 129.2, 128.6, 128.5, 128.4, 128.0 (10 arom. CH), 113.0 (2 CN), 54.7 (C), 54.4 (2 OCH_3), 36.8 (2 C) ppm. IR (KBr): υ = 2243 (w, C≡N), 1774 and 1761 (vs, C=O), 1451 (m), 1432 (m), 1268 (m), 1240 (s, br., O–C), 1144 (m), 1027 (w), 907 (w), 709 (m) cm^{-1}. EA for $C_{21}H_{16}N_2O_4$ (360.36): calcd. C 69.99, H 4.47, N 7.77; found C 69.81, H 4.54, N 7.52.

Reaction with 5-Diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (**2f**): An experiment was performed only with (*E*)-**1**; molar ratio (*E*)-**1**/**2f** = 1:3; reaction time 4 h. A colorless solid precipitated from the CH_2Cl_2 solution. After filtration, 190 mg of a colorless product were separated and crystallized from MeOH with a small admixture of CH_2Cl_2.

5,5'-Bi(10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptenylidene) (**5**): Colorless crystals, m.p. 315–318 °C (from MeOH/CH_2Cl_2); [ref.[12a] m.p. 291–292.5 °C]. ^{1}H NMR

($CDCl_3$): δ = 7.13–6.78 (3m, 16 arom. CH), 3.77–3.71 (m, 4 H, 2 CH_2), 3.08–3.03 (m, 4 H, 2 CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.9, 138.4 (8 arom. C), 140.0 (2 C_{sp2}), 129.1, 128.8, 126.7, 125.4 (16 arom. CH), 32.9 (4 CH_2) ppm. EA for $C_{30}H_{24}$ (384.51): calcd. C 93.71, H 6.29; found C 93.60, H 6.38.

Reaction with 5-Diazo-5*H*-dibenzo[*a,d*]cycloheptene (**2g**): An experiment was performed only with (*E*)-**1**; molar ratio (*E*)-**1/2g** = 1:3; reaction time 72 h. The crude product was purified chromatographically on plates coated with silica gel using petroleum ether/CH_2Cl_2 mixture (1:1) as an eluent.

1,2-Bis(10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)hydrazine (**6**): Yellow needles, m.p. 212–214 °C (from MeOH/CH_2Cl_2) [ref.[13c] m.p. 224–226 °C]. ^{1}H NMR ($CDCl_3$): δ = 7.66 (br., 2 H), 7.55 (br., 4 H), 7.40–7.30 (m, br., 8 H), 6.94 (br., 2 H), 6.74 (br. 4 H) ppm. IR (KBr): υ = 1647 (w, C=N), 1578 (m), 1325 (m), 954 and 942 (w), 800 (vs), 778 (vs), 729 (m) cm^{-1}. EA for $C_{30}H_{20}N_2$ (408.49): calcd. C 88.21, H 4.93, N 6.86; found C 87.79, H 5.01, N 6.92.

Reaction with (Trimethylsilyl)diazomethane (**2h**): Experiment A: molar ratio (*E*)-**1/2h** = 1:3 ; reaction time: 30 min. Experiment B: molar ratio (*Z*)-**1/2h** = 1:3; reaction time: 30 min. From both experiments only one product **7** in comparable yields of ca. 45% was isolated after filtration through a short chromatographic column filled with silica gel. Attempted aqueous work-up was not successful and no products were found in the separated, organic phase (CH_2Cl_2).

Methyl 4-Cyano-1-methyl-1*H*-pyrazole-5-carboxylate (**7**): Colorless crystal, m.p. 82–84 °C (from MeOH) (ref.[5] m.p. 84–86 °C). ^{1}H-NMR ($CDCl_3$): δ = 7.79 (1 arom. H, CH), 4.21 (3 H, OCH_3), 4.00 (3 H, NCH_3) ppm. ^{13}C-NMR ($CDCl_3$): δ = 158.1 (C=O), 141.8 (1 arom. CH), 135.3, 112.3 (2 arom. C), 96.7 (CN), 52.9 (OCH_3), 40.4 (NCH_3) ppm. IR (KBr): υ = 3140 and 3122 (w), 2959 (w), 2240 (s, C≡N), 1733 (vs, C=O), 1538 (m), 1485 and 1436 (s, br), 1274 (vs, O–C), 1116 (s), 1071 (m), 887 (m), 816 (m), 660 (m), 634 (w) 446 (w) cm^{-1}. EA for $C_7H_7N_3O_2$ (165.15): calcd. C 50.91, H 4.27, N 25.44; found C 50.61, H 4.33, N 25.59.

X-ray Crystal Structure Determination: Suitable single crystals of *trans*-**4c** and **7** were obtained by crystallization from MeOH solution. Single crystal X-ray data were collected with a Rigaku Oxford Diffraction XtaLAB Synergy, Pilatus 300K diffractometer (CuKα radiation, λ = 1.54178 Å, PhotonJet (Cu) X-ray Source with mirror) at 100.0 K. Using Olex2,[32] the structure was solved with the SHELXT[33] structure solution program using Intrinsic Phasing and refined with the SHELXL[34] refinement package using Least Squares minimization.

Crystal data for ***trans*-4c**: $C_{21}H_{14}N_2O_4$, M = 358.34, colorless, prism, crystal size 0.497 × 0.177 × 0.169 mm^3, monoclinic, space group $P2_1/c$, Z = 4, 2θ range for data collection 7.634 – 133.19°, a = 11.67620(10), b = 12.22460(10), c = 11.98520(10) Å, β = 97.3530(10)°, V = 1696.66(2) Å^3, T = 100.01(10) K, D_X = 1.403 g·cm^{-3}, μ(Cu$K\alpha$) = 0.816 mm^{-1}, scan type ω, total reflections measured 40839, symmetry independent reflections 2993, reflections used in refinement 2993, parameters refined 247, restraints 0, final R_1 [$I > 2\sigma(I)$ reflections] = 0.0302, wR_2 [all data] = 0.0726, goodness of fit on F^2 1.056, $\Delta\rho$ (max; min) = 0.23; –0.16 e Å^{-3}.

Crystal data for **7**: $C_7H_7N_3O_2$, M = 165.16, colorless, plates, crystal size 0.469 × 0.393 × 0.124 mm^3, monoclinic, space group $P2_1/n$, Z = 4, 2θ range for data collection 11.38 – 133.11°, a = 8.35080(10), b = 6.12240(10), c = 15.8558(2) Å, β = 101.2480(10)°, V = 795.087(19) Å^3, T = 100.00(10) K, D_X = 1.380 g·cm^{-3}, μ(Cu$K\alpha$) = 0.886 mm^{-1}, scan type ω, total reflections measured 15946, symmetry independent reflections 1400, reflections used in refinement 1400, parameters refined 112, restraints 0, final R_1 [$I > 2\sigma(I)$ reflections] = 0.0278, wR_2 [all data] = 0.0721, goodness of fit on F^2 1.061, $\Delta\rho$ (max; min) = 0.20; –0.18 e Å^{-3}.

The crystallographic data for ***trans*-4c** and **7** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-1565893 and 1565533. These data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223 336 033; email: deposit@ccdc.cam.ac.uk (or via http://www.ccdc.cam.ac.uk/conts/retrieving.html).

Computational details: All calculations reported in this paper were performed using "Prometheus" infrastructure in the ‘Cyfronet’ computational center in Cracow. Hybrid functional B3LYP with the 6-31++G(d), basis set included in the GAUSSIAN 09

package[34] was used. Recently we have established that the same level of theory illustrates well the molecular mechanisms of different multistep cycloaddition processes.[35–37] Global and local electronic properties of reactants were estimated according to the equations recommended by *Parr* and *Domingo*.[21,38,39] For structure optimization of the reactants and the reaction products, the *Berny* algorithm was applied. The transition states were verified by diagonalization of the Hessian matrix and by analysis of the internal reaction coordinates (IRC). The calculations were carried out for the simulated presence of toluene or nitromethane as the reaction medium (PCM model[40] was used). For optimized structures, the thermochemical data for the temperature T = 298 K and pressure p = 1 atm were computed using vibrational analysis data. Global electron density transfer (GEDT)[41] was calculated according to the formula:

$$GEDT = -\Sigma q_A$$

where q_A is the net charge and the sum is taken over all the atoms of the ethylene derivative used.

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References

[1] M. Regitz, H. Heydt, in: 1,3-Dipolar Cycloaddition Chemistry (Ed.: A. Padwa), Wiley, New York, **1984**, vol. 1, p. 393–558.

[2] G. Maas, in: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products (Eds.: A. Padwa, W. H. Pearson), Wiley, New Jersey, **2002**, p. 539–621.

[3] a) H. M. L. Davies, E. G. Antoulinakis, *Org. React.* **2001**, *57*, 1–326; b) N. M. Roda, D. N. Tran, C. Battilocchio, R. Labes, R. J. Ingham, J. M. Hawkins, S. V. Ley, *Org. Biomol. Chem*. **2015**, *13*, 2550–2554; c) I. K. Sideri, E. Voutyritsa, Ch.

G. Kokoto, *Org. Biomol. Chem*. **2018**, *16*, on-line (DOI: 10.1039/C8OB00725J; d) I. D. Jurberg, H. M. L. Davies, *Chem. Sci.* **2018**, 9, 5112–5118.

[4] G. Mlostoń, H. Heimgartner, *Beilstein J. Org. Chem.* **2017**, *13*, 2235–2251.

[5] a) R. Huisgen, A. Mitra, J. R. Moran, *Chem. Ber.* **1987**, *120*, 159–169; b) R. Huisgen, A. Mitra, J. R. Moran, *Heterocycles* **1986**, *24*, 2429–2436.

[6] G. Mlostoń, R. Huisgen, H. Giera, *Tetrahedron* **2002**, *58*, 4185–4193.

[7] R. Jasiński, K. Kula, A. Kącka, B. Mirosław, *Monatsh. Chem.* **2017**, *148*, 909–915.

[8] V. A. Vasin, Y. A. Popkova, E. V. Bezrukova, V. V. Razin, N. V. Somov, *Russ. J. Org. Chem.* **2017**, *53*, 393–397.

[9] L. R. Domingo, M. Rios-Gutiérrez, S. Emamian, *RSC Advances* **2017**, *7*, 15586–15595.

[10] O. A. Ivanova, E. M. Budymina, E. B. Averina, T. S. Kuznetsova, Y. K. Grishin, N. S. Zefirov, *Synthesis* **2007**, 2009–2013.

[11] L. R. Domingo, *Molecules* **2016**, *21*, 1319.

[12] a) I. Moritani, S.-I. Murahashi, K. Yoshinaga, H. Ashitaka, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1506–1511; b) J. Luo, K. Song, F. L. Gu, Q. Miao, *Chem. Sci.* **2011**, *2*, 2029–2034.

[13] a) S.-I. Murahashi, I. Moritani, M. Nishino, *J. Am. Chem. Soc.* **1967**, *89*, 1257–1259; b) S.-I. Murahashi, I. Moritani, M. Nishino, *Tetrahedron* **1971**, *27*, 5131–5145; c) M. I. Hegab, A. B. A. El-Gazzar, F. A. Gad, *Egypt. J. Chem.* **2001**, *44*, 355–366.

[14] W. Sucrow, D. Rau, A. Fehlauer, J. Pickardt, *Chem. Ber.* **1979**, *112*, 1719–1730.

[15] R. Huisgen, U. Eichenauer, E. Langhals, A. Mitra, J. R. Moran, *Chem. Ber.* **1987**, *120*, 153–158.

[16] E. Weber, M. Hecker, I. Csoeregh, M. Czugler, *J. Am. Chem. Soc.* **1989**, *111*, 7866–7872.

[17] Y. D. Samuilov, A. I. Movchan, S. E. Solov'eva, A. I. Konovalov, *Zh. Org. Khim.* **1984**, *20*, 2179–2182.

[18] R. Huisgen, E. Langhals, *Tetrahedron Lett.* **1989**, *30*, 5369–5372.

[19] a) L. R. Domingo, M. Rios-Gutierrez, P. Perez, *Tetrahedron* **2016**, *72*, 1524–1532; b) R. Jasiński, *Monatsh. Chem.* **2015**, *146*, 591–599.

[20] L. R. Domingo, M. J. Aurell, P. Perez, *Tetrahedron* **2014**, *70*, 4519–4525.

[21] L. R. Domingo, P. Perez, J. A. Saez, *RSC Adv*. **2013**, *3*, 1486–1494.

[22] a) J. W. Park, P. B. Mackenzie, W. P. Schaefer, R. H. Grubbs, *J. Am. Chem. Soc.* **1986**, *108*, 6402–6404; b) R. Huisgen, G. Mlostoń, E. Langhals, *J. Org. Chem.* **1986**, *51*, 4085–4087; c) M. Woźnicka, M. Rutkowska, G. Mlostoń, A. Majchrzak, H. Heimgartner, *Pol. J. Chem.* **2006**, *80*, 1683–1693.

[23] T. Aoyama, Y. Iwamoto, S. Nishigaki, T. Shioiri, *Chem. Pharm. Bull.* **1989**, *37*, 253–256.

[24] H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151–1196.

[25] S. Zhu, X. Xu, J. A. Perman, X. P. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12796–12799.

[26] G. Mloston, M. Celeda, H. Heimgartner, *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 207–210.

[27] R. S. Muthyala, S. Sheng, K. E. Carlson, B. S. Katzenellenbogen and J. A. Katzenellenbogen, *J. Med. Chem.*, **2003**, *46*, 1589–1602.

[28] a) W. Chew, R. C. Hynes, D. N. Harpp, *J. Org. Chem.*, **1993**, *58*, 4398–4404; (b) B. B. Wright, M. S. Platz, *J. Am. Chem. Soc*. **1984**, *106*, 4175–4180.

[29] P. Costa, T. Lohmiller, I. Trosien, A. Savitsky, W. Lubitz, M. Fernandez-Oliva, E. Sanchez-Garcia, W. Sander, *J. Am. Chem. Soc.* **2016**, *138*, 1622–1629.

[30] Mlostoń, P. Grzelak, R. Hamera-Fałtyga, M. Jasiński, K.Urbaniak, P. Pipiak, Ł. Albrecht, J. Hejmanowska, H. Heimgartner, *Phosphorus Sulfur Silicon Relat. Elem.* **2017**, *192*, 204−211.

[31] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341.

[32] G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3–8.

[33] G. M. Sheldrick, *Acta Cryst C* **2015**, *71*, 3–8.

[34] M. J. Frisch , G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Jr. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, Y. Nakajima, O. Honda, O. Kitao, H. Nakai, M. Klene, X Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, M. C., Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G.

Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez,. J. A. Pople, Gaussian 09 rev A.1 Gaussian, Inc. Wallingford CT, (2009).

[35] R. Jasiński, *Comp. Theoret. Chem.* **2018**, *1125*, 77–85.

[36] R. Jasiński, *J. Mol. Graph. Model.* **2017**, *75*, 55–61.

[37] R. Jasiński, M. Zmigrodzka, E. Dresler, K. Kula, *J. Heterocyclic Chem.* **2017**, *54*, 3314–3320.

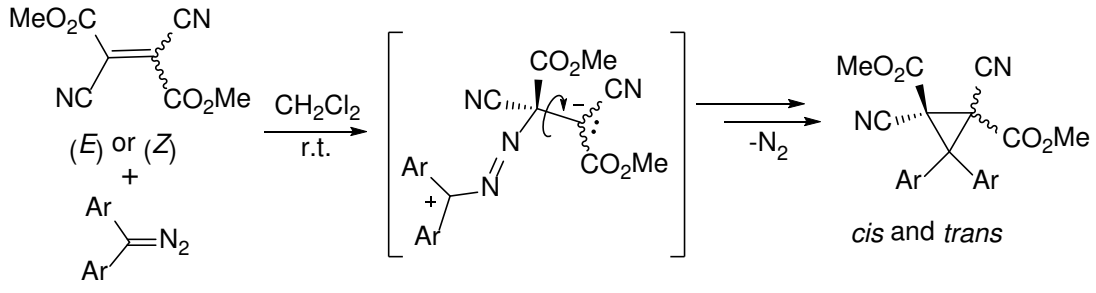
[38] P. Pérez, L. R. Domingo, A. Aizman, R. Contreras, in Toro-Labbe, A. (Ed.), *Theor. Aspects Chem. React*. **2008**, *19*, 139–201.

[39] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University, New York (1989).

[40] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* **2003**, *24*, 669–681.

[41] L. R. Domingo, *RSC Adv.* **2014**, *4*, 32415–32428.

Graphical abstract:



Textual abstract:

Isomeric, electron deficient dimethyl dicyanofumarate and dimethyl dicyanomaleate react with bis(4-methoxyphenyl)diazomethane, diphenyldiazomethane and 9-diazofluorene at room temperature in CH_2Cl_2 solutions to give, after spontaneous

extrusion of N_2, mixtures of dimethyl *cis*- and *trans*-3,3-diaryl-1,2-dicyano-cyclopropane-1,2-dicarboxylates. The proposed stepwise mechanism of the reaction was rationalized on the basis of a computational study.